HFO-1234yf Low GWP Refrigerant for MAC Applications

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Barbara Minor

Engineering Fellow

DuPont Fluoroproducts

Mobile Air Conditioning Climate Protection Partnership Meeting

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Background

DuPont And Honeywell Have Identified HFO-1234yf ($CF_3CF=CH_2$) As The Preferred Low GWP Refrigerant Which Offers The Best Balance Of Properties And Performance

Other Auto Industry Options Have Certain Limitations

- CO_2 : complexity, energy efficiency and requires mitigation
- 152a / secondary loop: performance, size and weight

HFO-1234yf – The Leading Alternative Refrigerant to Replace R-134a

Excellent environmental properties

- Very low GWP of 4, Zero ODP, Favorable LCCP
- Atmospheric chemistry determined and published

Low toxicity, similar to R-134a

- Low acute and chronic toxicity

System performance very similar to R-134a

- Excellent COP and Capacity, no glide
  - From both internal tests and OEM tests
- Thermally stable and compatible with R-134a components
- Potential for direct substitution of R-134a

Mild flammability (manageable)

- Flammability properties significantly better than 152a; (MIE, burning velocity, etc)
- Potential for “A2L” ISO 817 classification versus “A2” for 152a based on AIST data
- Potential to use in a direct expansion A/C system

Global Solution

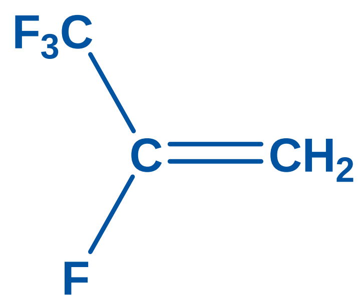
- Lowest total cost of transition than any alternative
- good performance in all climates, and car sizes

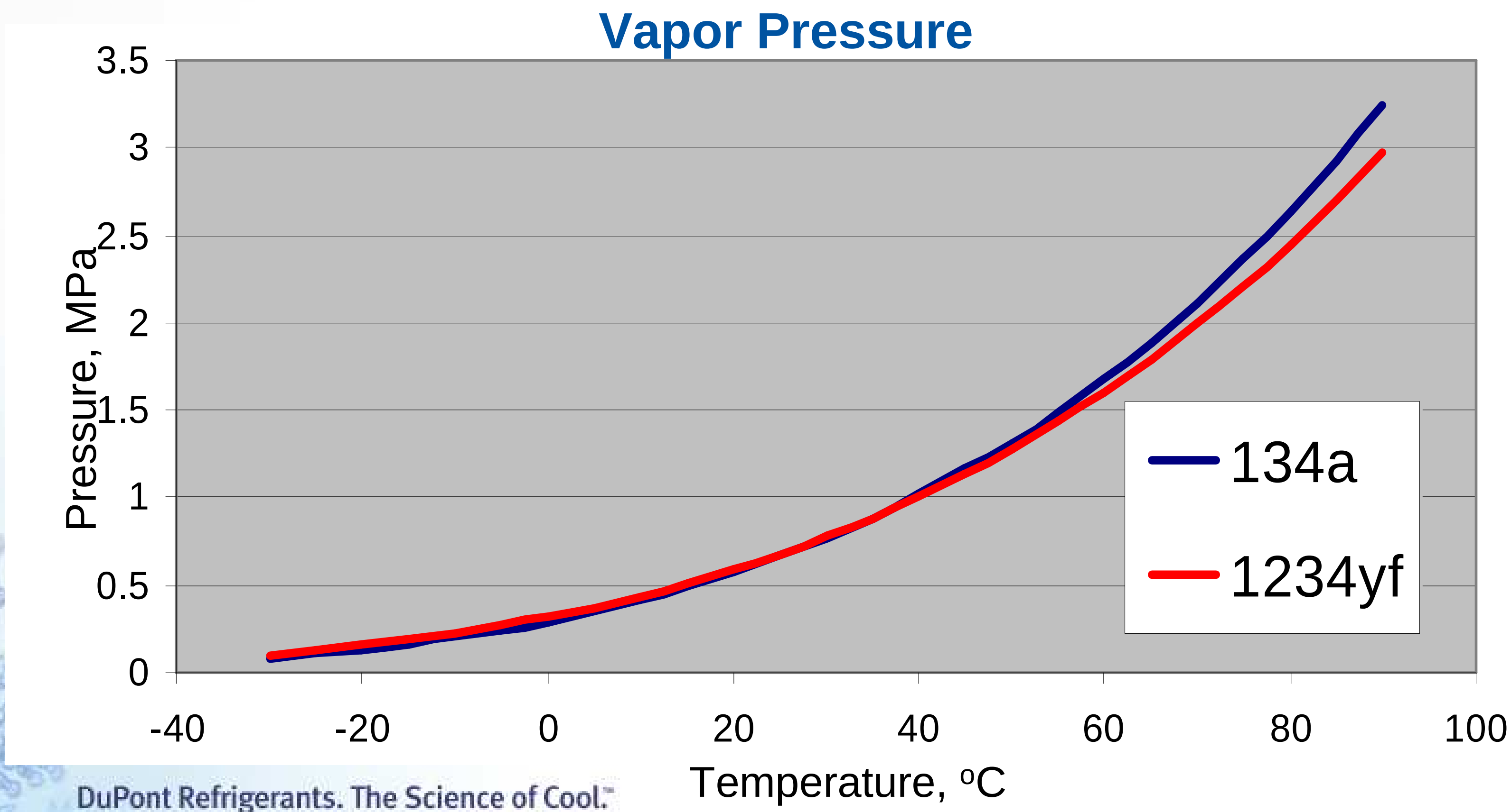
HFO-1234yf Properties

Properties	1234yf	134a
Boiling Point, T_b	**-29°C**	**-26°C**
Critical Point, T_c	**95°C**	**102°C**
P_{vap}, MPa (25°C)	**0.673**	**0.665**
P_{vap}, MPa (80°C)	**2.47**	**2.63**
Liquid Density, kg/m³ (25°C)	**1094**	**1207**
Vapor Density, kg/m³ (25°C)	**37.6**	**32.4**

1234yf

$CF_3CF=CH_2$





HFO-1234yf - Excellent Environmental Properties

ODP = 0

100 Year GWP = 4 **(GWP_{134a} = 1430)**

- Measurements completed & published

Atmospheric lifetime = 11 days

Atmospheric chemistry measured

- Atmospheric breakdown products are the same as for 134a
- No high GWP breakdown products (e.g. **NO** HFC-23 breakdown product)
- Results published in 2008

Published Papers

•Papadimitrou, V.C. et al, **"$CF_3CF{=}CH_2$ and Z-$CF_3CF{=}CHF$: Temperature dependent OH rate coefficients and global warming potentials",** *Phys. Chem. Chem. Phys*. Vol 10 (2008) pp 808-820.

•Hurley, M.D. et al, **"Atmospheric chemistry of $CF_3CF{=}CH_2$: Products and mechanisms of Cl atom and OH radical initiated oxidation",** *Chem. Phys. Lett*. Vol 450 (2008) pp 263-267.

•Nielsen, O.J. et al, **"Atmospheric Chemistry of $CF_3CF{=}CH_2$: Kinetics and mechanisms of gas phase reactions with Cl atoms, OH radicals and O_3",** *Chem. Phys. Lett*. Vol 439 (2007) pp 18-22.

HFO-1234yf Toxicity Results

Test	HFO-1234yf	R134a	
Acute Lethality	No deaths 400,000 ppm	No deaths 359,700 ppm	✓
Cardiac sensitization	NOEL > 120,000 ppm	NOEL 50,000 ppm LOEL 75,000 ppm	✓
13 week inhalation	NOAEL 50,000 ppm	NOAEL 50,000 ppm	✓
Developmental (Rat)	NOAEL 50,000 ppm	NOAEL 50,000 ppm	✓
Genetic Toxicity	Not Mutagenic	Not Mutagenic	✓
13 week genomic (carcinogenicity)	Not active (50,000 ppm)	Not tested	✓
2-yr carcinogenicity	Not required (see genomics)	Not carcinogenic	
Environmental Tox	NOEL > 83 mg/L (Pass)	NOEL > 100 mg/L (Pass)	✓
Developmental (Rabbit)	NOAEL 4,000 PPM, LOAEL 5,500 PPM	NOAEL 2,500 PPM LOAEL 10,000	✓
1-Gen segment of 2-Gen Reproductive	Interim NOAEL 5,000 ppm (6-hours exposures)	NOAEL 50,000ppm (1-hour exposures)	✓

HFO-1234yf Has Low Toxicity

ATEL Calculation –Short Term Exposure

ATEL (Acute Toxicity Exposure Limit) is a value used by standards organizations (e.g. ASHRAE 34) to reduce the risks of acute toxicity hazards in normally occupied spaces.

It is calculated from the acute toxicity data for a given refrigerant and provides an estimate of the maximum exposure limit for a short time period (e.g. 30 minutes)

Refrigerant	ATEL (ppm)
R-12	18,000
R-134a	50,000
R-152a	50,000
CO_2	40,000
HFO-1234yf	101,000

HFO-1234yf Has a Favorable ATEL Value

HFO-1234yf: Excellent Plastics Compatibility

ND8 PAG at 100℃ for two weeks

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
HFO-1234yf	Polyester	1	4.4	0
"	Nylon	1	-1.5	1
"	Epoxy	1	0.3	1
"	Polyethylene Terephthalate	1	2.0	0
"	Polyimide	0	0.2	0

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
R134a	Polyester	1	5.6	0
"	Nylon	1	-1.4	1
"	Epoxy	1	0.3	1
"	Polyethylene Terephthalate	1	2.8	0
"	Polyimide	0	0.7	0

Rating 0 = best when weight gain < 1 and physical change = 0
1 = borderline when weight gain > 1 and < 10 and/or physical change upto 2
2 = incompatible when weight gain > 10 and/or physical change = 2

HFO-1234yf: Excellent Elastomers Compatibility

ND8 PAG at 100℃ for two weeks

Refrigerant	Elastomers	Rating	24 h Post Linear Swell %	24 h Post Weight Gain %	24 h Post Delta Hardness
HFO-1234yf	Neoprene WRT	0	0.0	-0.3	1.0
"	HNBR	0	1.6	5.5	-7.0
"	NBR	0	-1.2	-0.7	4.0
"	EPDM	0	-0.5	-0.6	4.0
"	Silicone	1	-0.5	2.5	-14.5
"	Butyl rubber	0	-1.6	-1.9	0.5

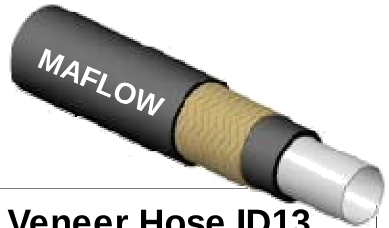
Refrigerant	Elastomers	Rating	24 h Post Linear Swell %	24 h Post Weight Gain %	24 h Post Delta Hardness
R134a	Neoprene WRT	0	-0.6	-1.3	2
"	HNBR	0	2.1	8.6	-5.5
"	NBR	0	0.0	3.0	-3.5
"	EPDM	0	-1.1	-0.4	-2
"	Silicone	0	-1.4	1.4	-2.5
"	Butyl rubber	0	-1.1	-1.6	-3.5

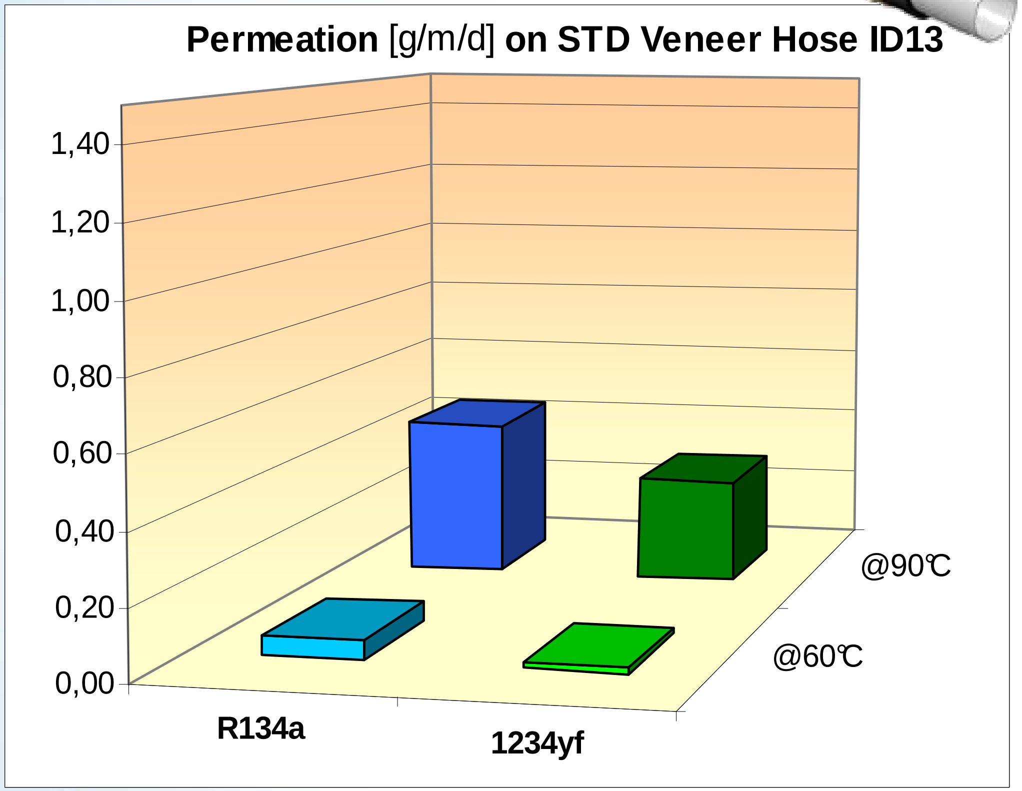
Rating

0 = best when weight gain < 1 and physical change = 0
1 = borderline when weight gain > 1 and < 10 and/or physical change upto 2
2 = incompatible when weight gain > 10 and/or physical change = 2

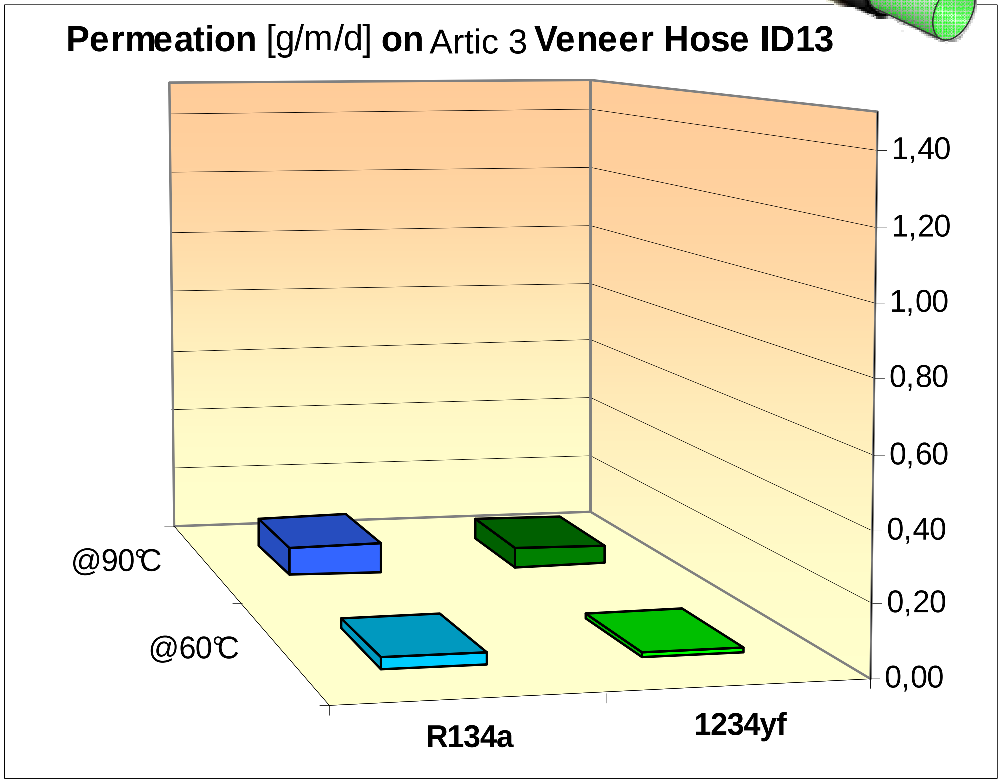
Permeation HFO-1234yf vs R-134a

Standard Veneer Hose





ULEV Veneer Hose



Results

HFO-1234yf shows lower permeability values toward Veneer hoses compared to R134a.

With the same gas concentration (0.6g/cm³) the inner pressure with HFO-1234yf is lower (e.g: at 90℃ was -20%)

Refrigerant Flammability Tests

Is it flammable? If yes, Flame Limits will exist.

- LFL – lower flammability limit
- UFL – upper flammability limit

What is the probability of an ignition source being present of sufficient energy to cause an ignition?

- Autoignition temperature
- Minimum ignition energy (MIE)

What is the impact (damage potential) if an ignition occurs?

- Heat of combustion
- Burning velocity

HFO-1234yf Flame Limits

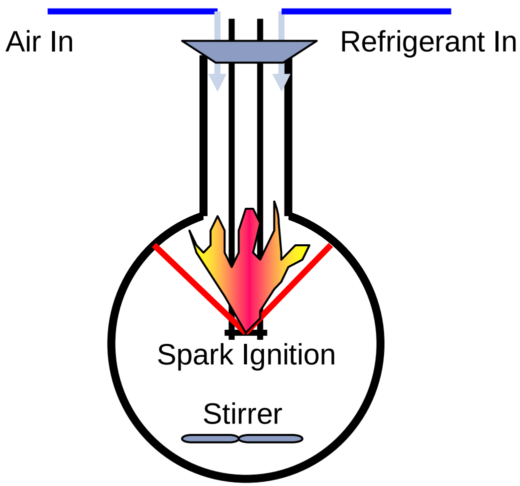
LFL Values

Ammonia	15 vol.%
HFC-32	13.3 vol.%
HFO-1234yf	**6.2 vol.%**
Methane	4.6 vol.%
HFC-152a	3.9 vol.%
Ethylene Oxide	3.0 vol.%
Acetylene	2.5 vol.%
Propane	2.1 vol.%
Gasoline	1.6 vol.%

More Flammable

- HFO-1234yf flame limits measured using ASTM E681-04 T= 21ºC : 6.2 vol.% to 12.3 vol.%
- **Low LFL value → more flammable**
- Wider UFL – LFL → more flammable

ASTM E681 Apparatus



- ASTM E-681 in US
  - 2004 version cited by ASHRAE (12 liter flask, spark ignition)
  - Flame must reach the wall and exhibit > 90 degree angle
  - 1985 version cited by SAE (5 liter flask, match ignition)
- A11 in EU
  - 5 cm x 30 cm Vertical tube
  - Spark ignition
  - Flame travels up the tube

HFO-1234yf Is Less Flammable Than 152a

Burning Velocity

National Institute of Advanced Industrial Science and Technology AIST

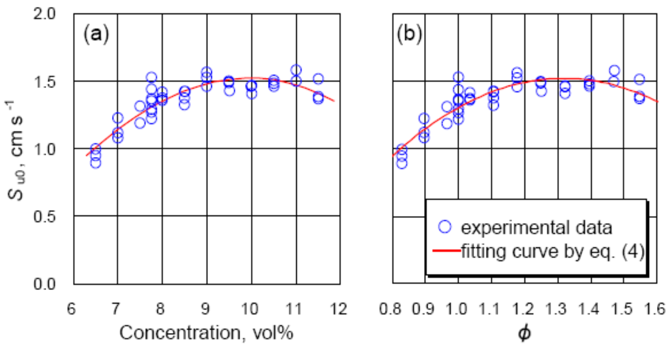
Final Technical Report on Flammability Assessment of 1234yf

Kenji Takizawa

National Institute of Advanced Industrial Science and Technology (AIST)

AIST

Burning velocity as a function of (a) concentration and (b) equivalence ratio



By fitting all the data to a paraboric function (4), maximum S_{u0} was obtained as 1.52 cm s^{-1} at ϕ =1.32. Therefore, the maximum S_{u0} is 1.5 cm s^{-1} at ca. 10 vol%.

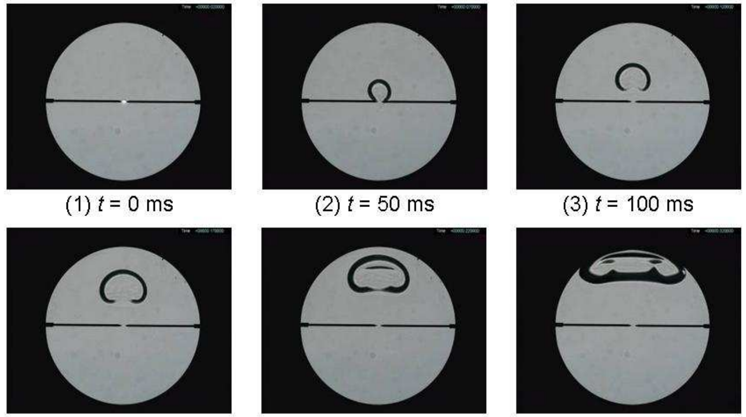
$$S_{u0} = S_{u0,max} + s_1 (\phi - \phi_{max})^2 \qquad (4)$$
$$= 1.52 - 2.13 (\phi - 1.32)^2$$

Appendix

AIST

Example of schlieren photography method

1234yf, 7.75 % (ϕ = 1), P_0 = 760 Torr, T_0 =291.45 K



(1) t = 0 ms (2) t = 50 ms (3) t = 100 ms

(4) t = 150 ms (5) t = 200 ms (6) t = 300 ms

Flame radii in the horizontal direction (r_f) were measured to minimize the effect of buoyancy. In this case I used the data from t = 50 to 150 ms, during which the flame front was not affected by any objects.

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Burning Velocity Measurements

Measurements performed in 3 liter spherical apparatus

Experimental result for HFO-1234yf: 1.5 cm s^{-1}

ISO 817 Flammability Classification is 2L (lowest flammable class classification)

	Propane	152a	NH_3	32	1234yf
BV, cm s^{-1}	16	23	7.2	6.7	**1.5***

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Minimum Ignition Energy

12-liter glass sphere used in ASTM E681 flammability limit tests was modified for MIE testing in order to eliminate potential wall quenching effects seen in standard 1 liter vessel

Materials Tested:

- HFC-32 from 16-22% (v/v) in 1% increments at 30 and 100 mJ nominal
- HFO-1234yf from 7.5-11% (v/v) in 0.5% increments up to 1000 mJ nominal
- Ammonia at 22% (v/v) at 100 and 300 mJ nominal

Refrigerant	***No Ignition Occurred***	***Ignition Occurred***
HFC-32	**30 +/- 12 mJ**	**100 +/- 30 mJ**
Ammonia	**100 +/- 30 mJ**	**300 +/- 100 mJ**
HFO-1234yf	**5,000 +/- 350 mJ**	**10,000 +/- 350 mJ**

HFO-1234yf Is Very Difficult To Ignite With Electrical Spark

HFO-1234yf Mild Flammability Properties

Flammability Properties

	LFL[a] (vol%)	UFL[a] (vol%)	Δ (vol%)	MIE (mJ)	BV[c] (cm/s)
Propane	**2.2**	**10.0**	**7.8**	**0.25**	**46**
R152a	**3.9**	**16.9**	**13.0**	**0.38**	**23**
R32	**14.4**	**29.3**	**14.9**	**30-100[b]**	**6.7**
Ammonia	**15**	**28**	**13**	**100-300[b]**	**7.2**
HFO-1234yf	**6.2**	**12.3**	**6.1**	**5,000-10,000[b]**	**1.5**

[a]Flame limits measured at 21 C, ASTM 681-01
[b]Tests conducted in 12 litre flask to minimize wall quenching effects
[c]Burning Velocity ISO 817 (HFO-1234yf BV measured by AIST, Japan)

Flammability Index

	R	F	RF	RF2
HFO-1234yf	0.97	0.27	3.6	0.6
32	1.31	0.33	4.6	2.3
152a	1.78	0.5	16.6	17.9
Propane	1.99	0.55	56.7	37.2

$$R = \frac{Cst}{LFL}$$

$$F = 1 - \sqrt{\left(\frac{LFL}{UFL}\right)}$$

$$RF = \left[\sqrt{\left(\frac{UFL}{LFL}\right)} - 1\right] \times \frac{Q}{M}$$

$$RF2 = \left\{\left(\sqrt{(UFL \times LFL)} - LFL\right) / LFL\right\} \times Qst \times Su$$

Cst = *Stoichiometric composition in air, vol.%*

Q = *Heat of Combustion per one mole*

Qst = *Heat of Combustion per one mole of the Stoichiometric mixture, kJ/mol*

Su = *Burning speed in Meters/Second*

M = *Molecular weight*

Autoignition Temperature & Hot Surface Ignition

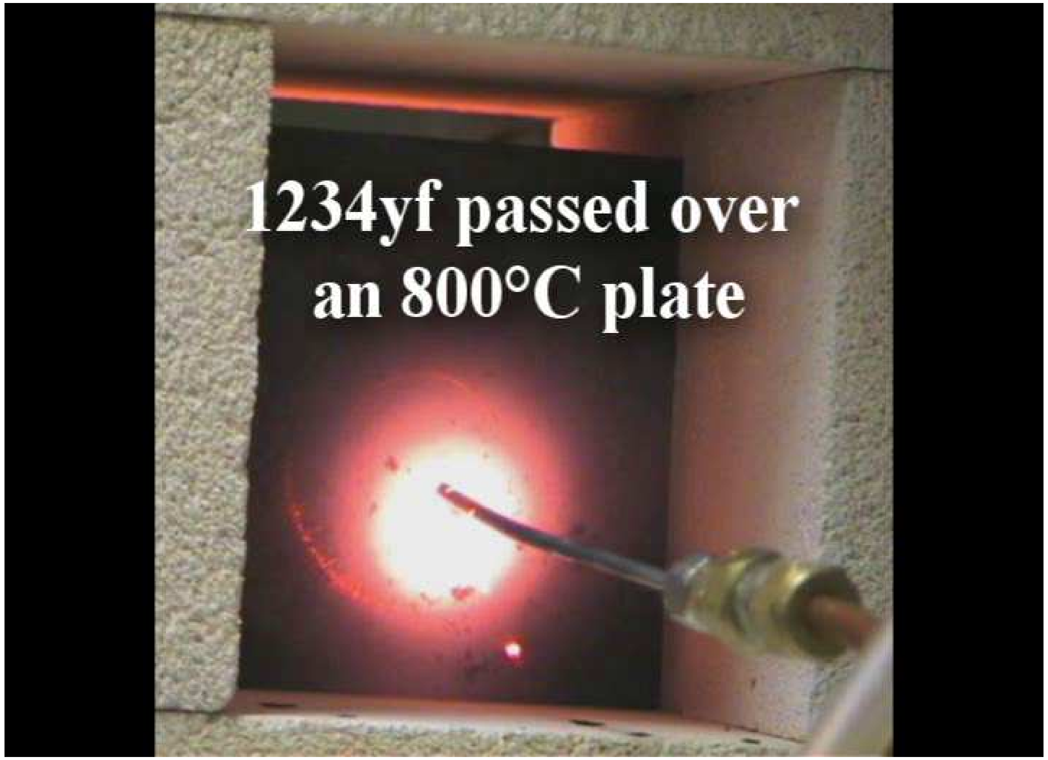
The autoignition temperature of HFO-1234yf was determined at Chilworth Technology in UK.

- **Uniformly heated 500 ml glass flask, observed in dark for 10 mins.**
- **Autoignition temperature for HFO-1234yf determined to be 405°C.**

Note that the air refrigerant mixture must be at this temperature for ignition to occur.

Experiments were conducted to evaluate the ignition potential of hot surfaces (up to 800°C) to cause ignition.

- **6 mm steel plate heated from behind with propane-oxygen torch**
- **No ignition seen**



- HFO-1234yf vapor sprayed onto the plate
- Infrared Thermometer measured temperature.
  - Three “dots” seen are to aim the thermometer
- Occasional red circles are diffraction rings from the camera lens reflecting the red plate through the refractive index gradient (caused by hot air / cold refrigerant).

Summary of Hot Plate Tests

		Hot Manifold		
		550°C Faint Red	800°C Cherry Red	>900°C Orange
HFO-1234yf	Spray No oil	No ignition	No ignition	No ignition
	Premixed with air no oil	Not tested	No ignition	No ignition
	with PAG oil	No ignition	No ignition	Ignition
R-134a	Spray no oil	No ignition	No ignition	No ignition
	Premixed with air no oil	Not tested	No ignition	No ignition
	with PAG oil	No ignition	No ignition	Ignition

HFO-1234yf shows same flammability behavior as R-134a - Ignition due to presence of oil

HFO-1234yf Ignitability to Spark from 12-V Battery Short Circuit

Determine whether a spark caused by a short circuit from a 12-V battery located under the seat is capable of igniting an 'optimum' concentration of HFO-1234yf in air

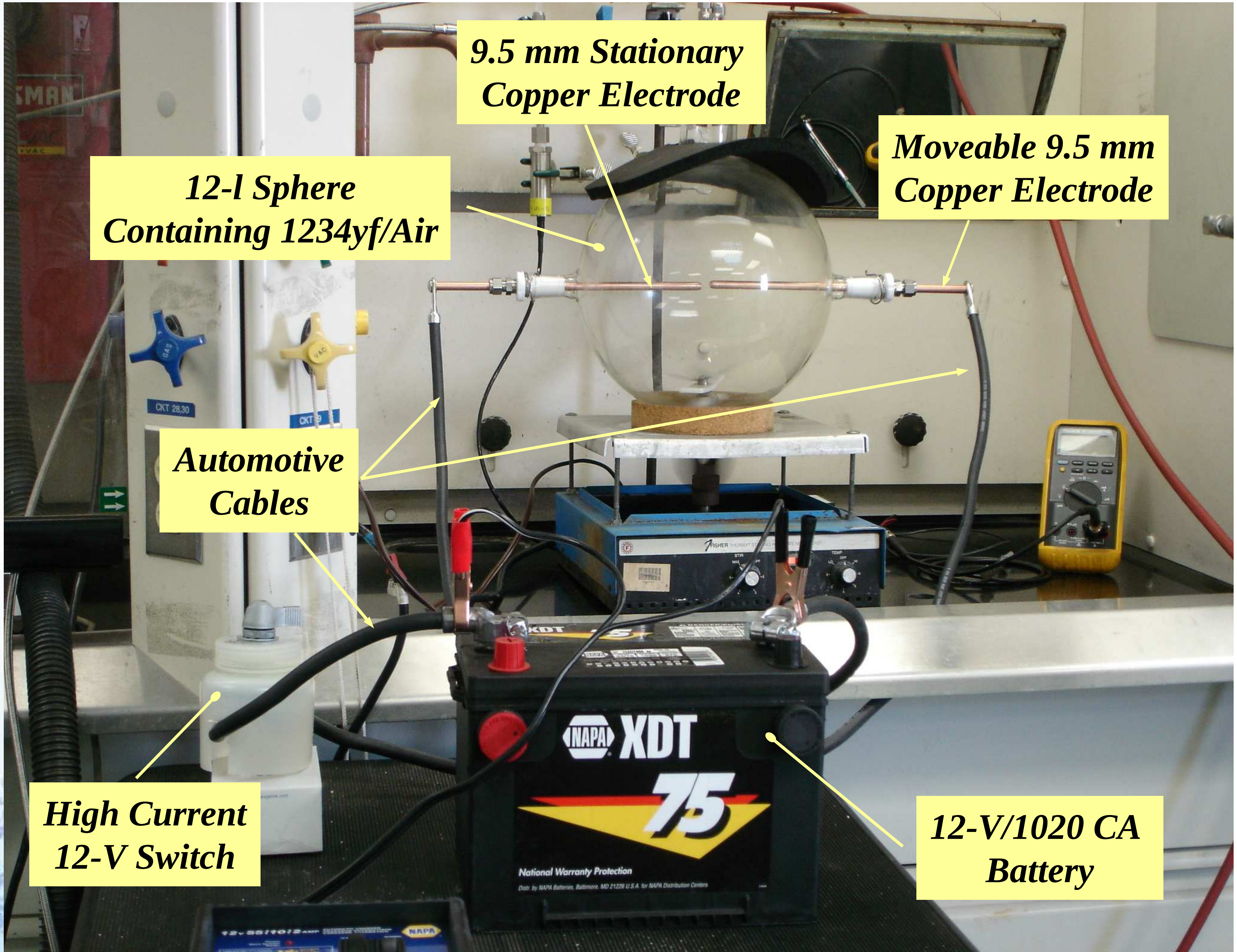
Follow procedures from ASTM E681 in a sealed 12- liter spherical flask; add moisture equivalent to 50% RH at 23^{o} C

Create a short-circuit in the mixture by discharging a high-capacity 12-V automotive battery (1020 cranking amps) across 9.5 mm diameter copper electrodes located in the sphere

<u>No ignitions</u> observed at 8.13, 8.5, and 9.0% HFO-1234yf worst case concentrations at either 20^{o}, 60^{o} or 80℃ (10 trials per concentration)

For comparison, the ignitability of <u>ammonia</u> was tested at a 20% v/v concentration at 20℃ and 60 ^{o} C; <u>ignition was obtained on the first trial</u>

Battery Ignition Apparatus



Sanden HFO-1234yf Performance Optimization Bench Tests

Tests conducted

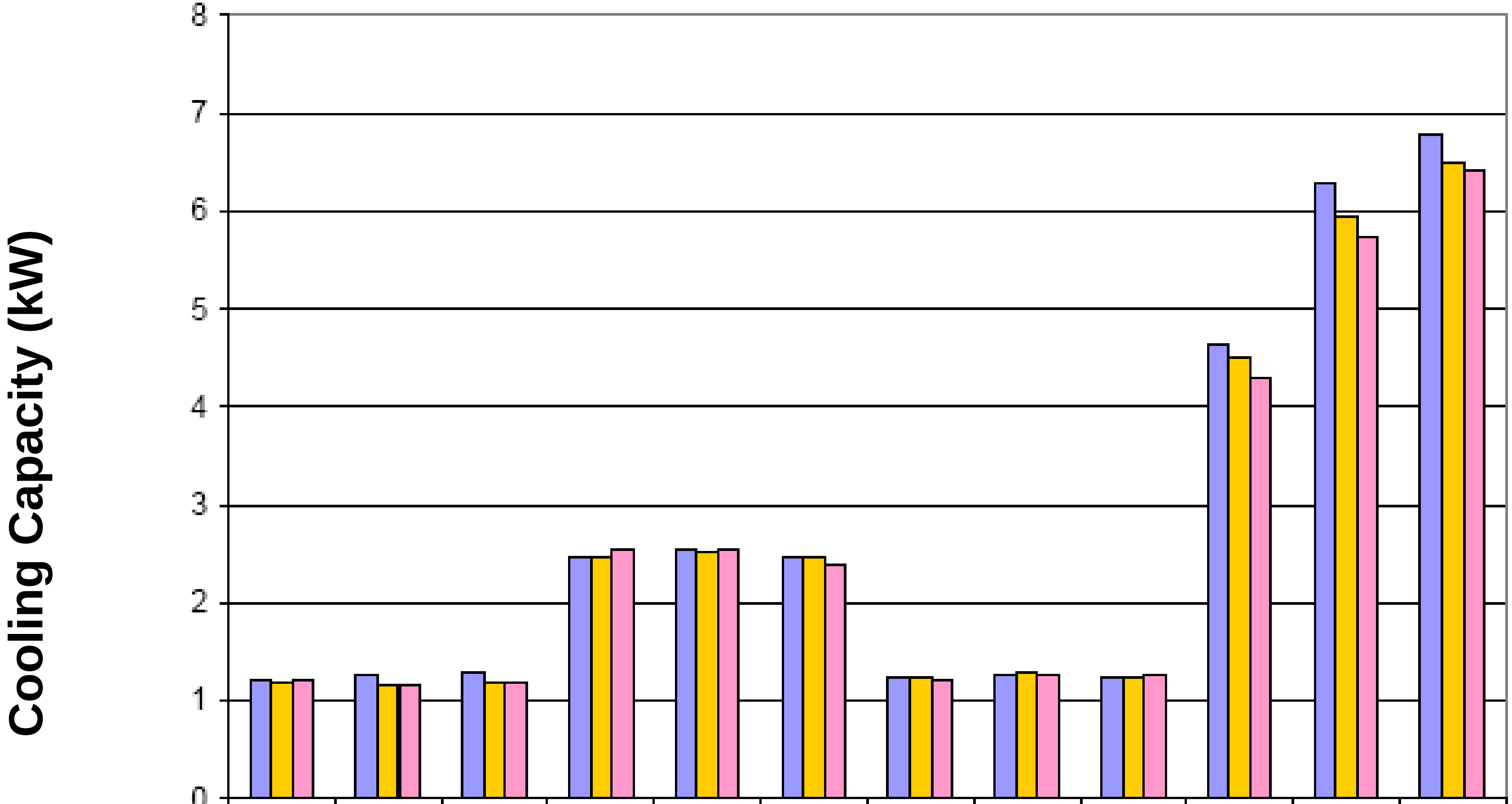
- R-134a Baseline
- HFO-1234yf drop-in with no changes
- HFO-1234yf with TXV adjustment
- HFO-1234yf with modified TXV by Fujikoki

Sanden Test Matrix

Test Conditions

Point	n_V [1/min]	t_{CL1} [℃]	t_{0L1} [℃]	m_{CL} [kg/h]	m_{0L} [kg/h]	φ_{oL1} [% rel.H.]	Target Temperature
1.1	800	25	25	750	175	50	t_{0L2}=8℃
1.2	1500	25	25	1200	175	50	t_{0L2}=8℃
1.3	2500	25	25	2200	175	50	t_{0L2}=8℃
2.1	800	25	25	750	350	50	t_{0L2}=8℃
2.2	1500	25	25	1200	350	50	t_{0L2}=8℃
2.3	2500	25	25	2200	350	50	t_{0L2}=8℃
3.1	800	40	25	750	175	50	t_{0L2}=8℃
3.2	1500	40	25	1200	175	50	t_{0L2}=8℃
3.3	2500	40	25	2200	175	50	t_{0L2}=8℃
4.1	800	40	40	750	350	50	max PWM
4.2	1500	40	40	1200	350	50	max PWM
4.3	2500	40	40	2200	350	50	max PWM

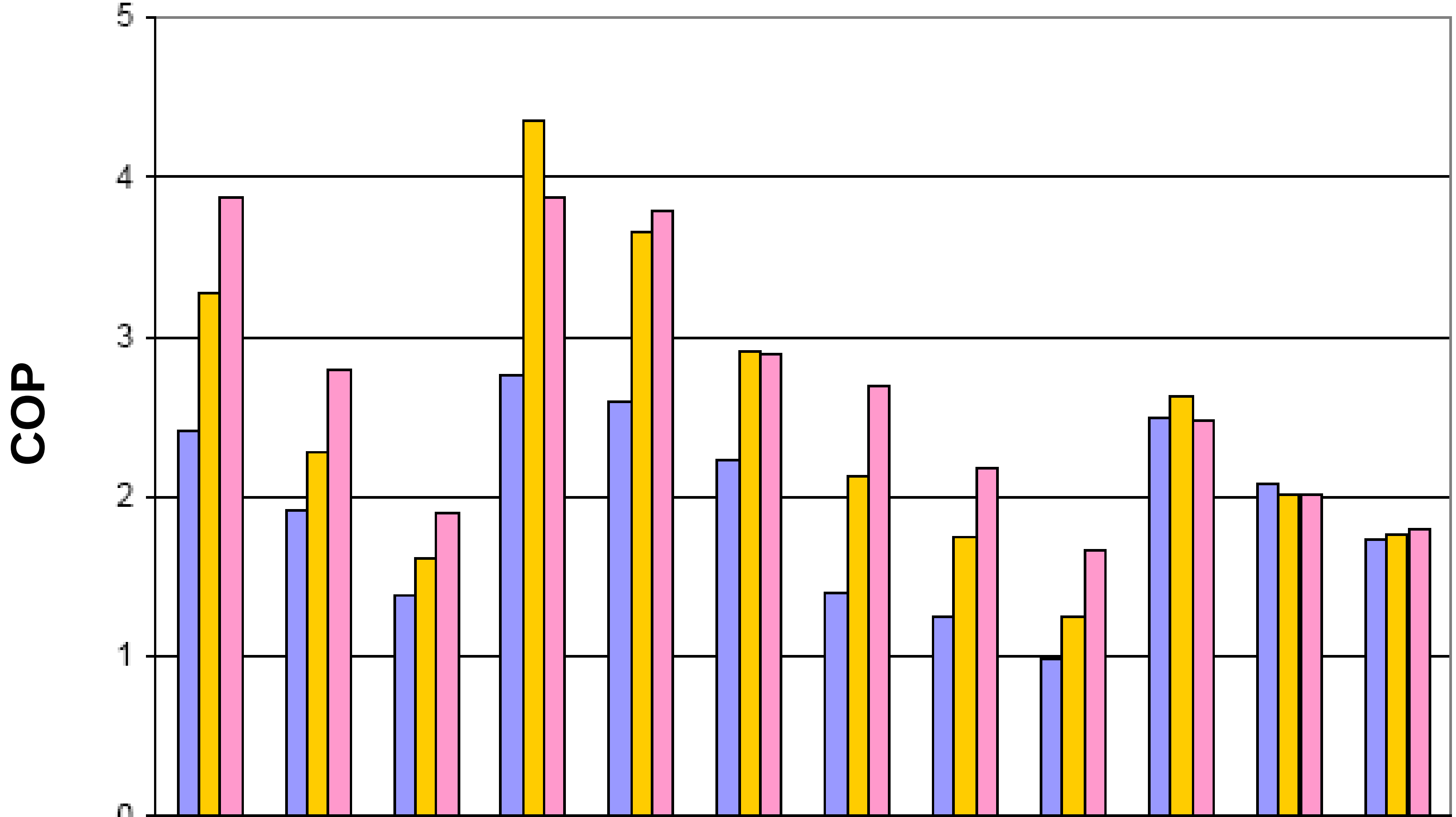
Sanden Test Results - Capacity



	1,1	1,2	1,3	2,1	2,2	2,3	3,1	3,2	3,3	4,1	4,2	4,3
R134a	1,21	1,26	1,28	2,48	2,54	2,48	1,25	1,26	1,23	4,64	6,28	6,78
R1234yf	1,18	1,16	1,19	2,48	2,52	2,47	1,24	1,29	1,24	4,52	5,94	6,49
R1234yf TXV	1,20	1,17	1,18	2,56	2,54	2,40	1,21	1,26	1,27	4,30	5,74	6,41

Cooling capacity similar to R-134a

Sanden Test Results - COP



	1,1	1,2	1,3	2,1	2,2	2,3	3,1	3,2	3,3	4,1	4,2	4,3
R134a	2,42	1,91	1,39	2,76	2,59	2,23	1,40	1,25	0,99	2,49	2,07	1,74
R1234yf	3,28	2,27	1,61	4,35	3,65	2,91	2,14	1,74	1,25	2,63	2,02	1,76
R1234yf TXV	3,87	2,79	1,90	3,88	3,79	2,89	2,69	2,17	1,67	2,49	2,01	1,81

COP improved versus R-134a

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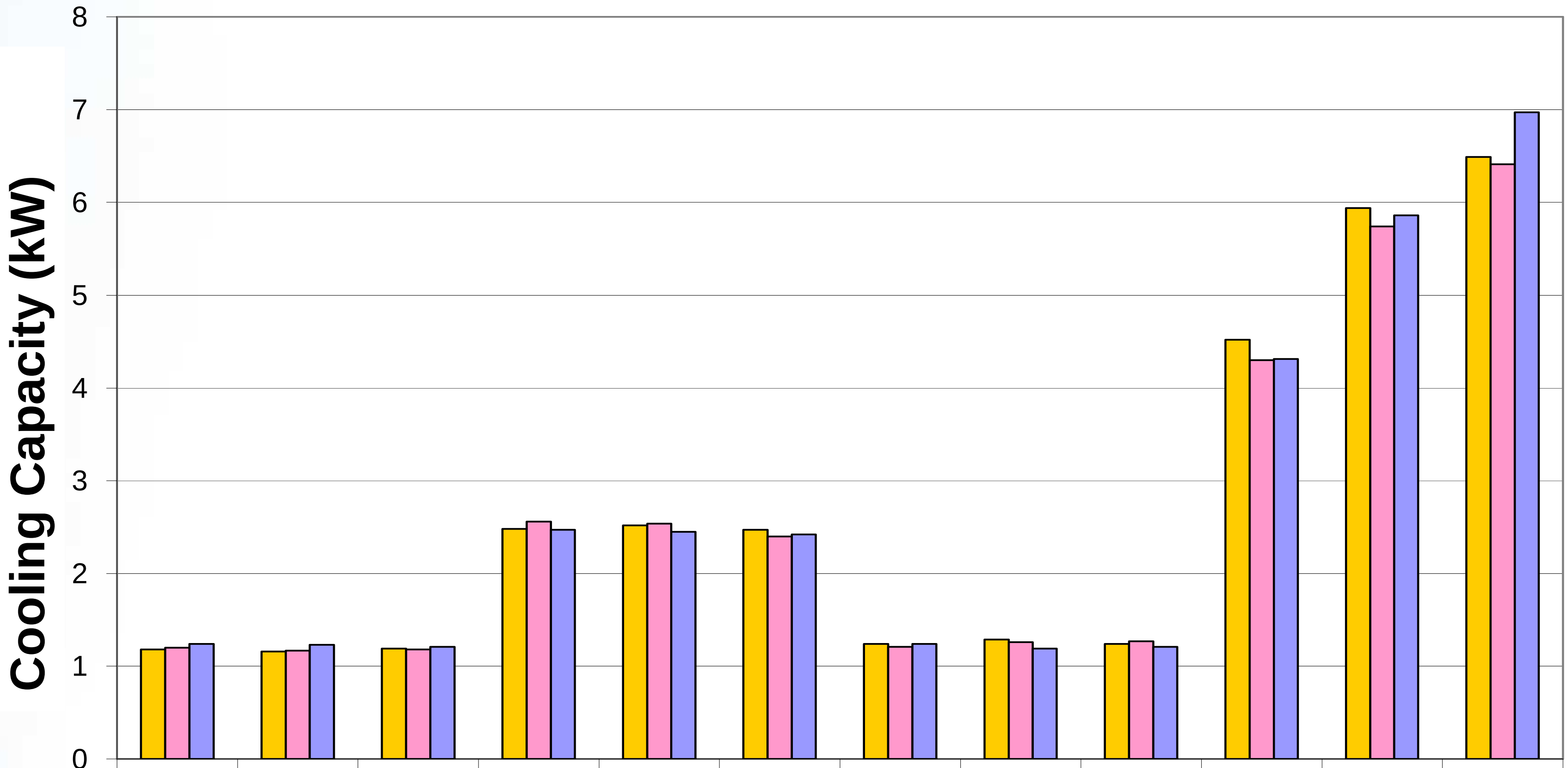
Sanden Bench Test
Capacity with Modified TXV



	1,1	1,2	1,3	2,1	2,2	2,3	3,1	3,2	3,3	4,1	4,2	4,3
Original TXV	1,18	1,16	1,19	2,48	2,52	2,47	1,24	1,29	1,24	4,52	5,94	6,49
TXV modi. manual	1,20	1,17	1,18	2,56	2,54	2,40	1,21	1,26	1,27	4,30	5,74	6,41
TXV 2.0t Fujikoki	1,24	1,23	1,21	2,47	2,45	2,42	1,24	1,19	1,21	4,31	5,86	6,97

Cooling capacity similar to R-134a

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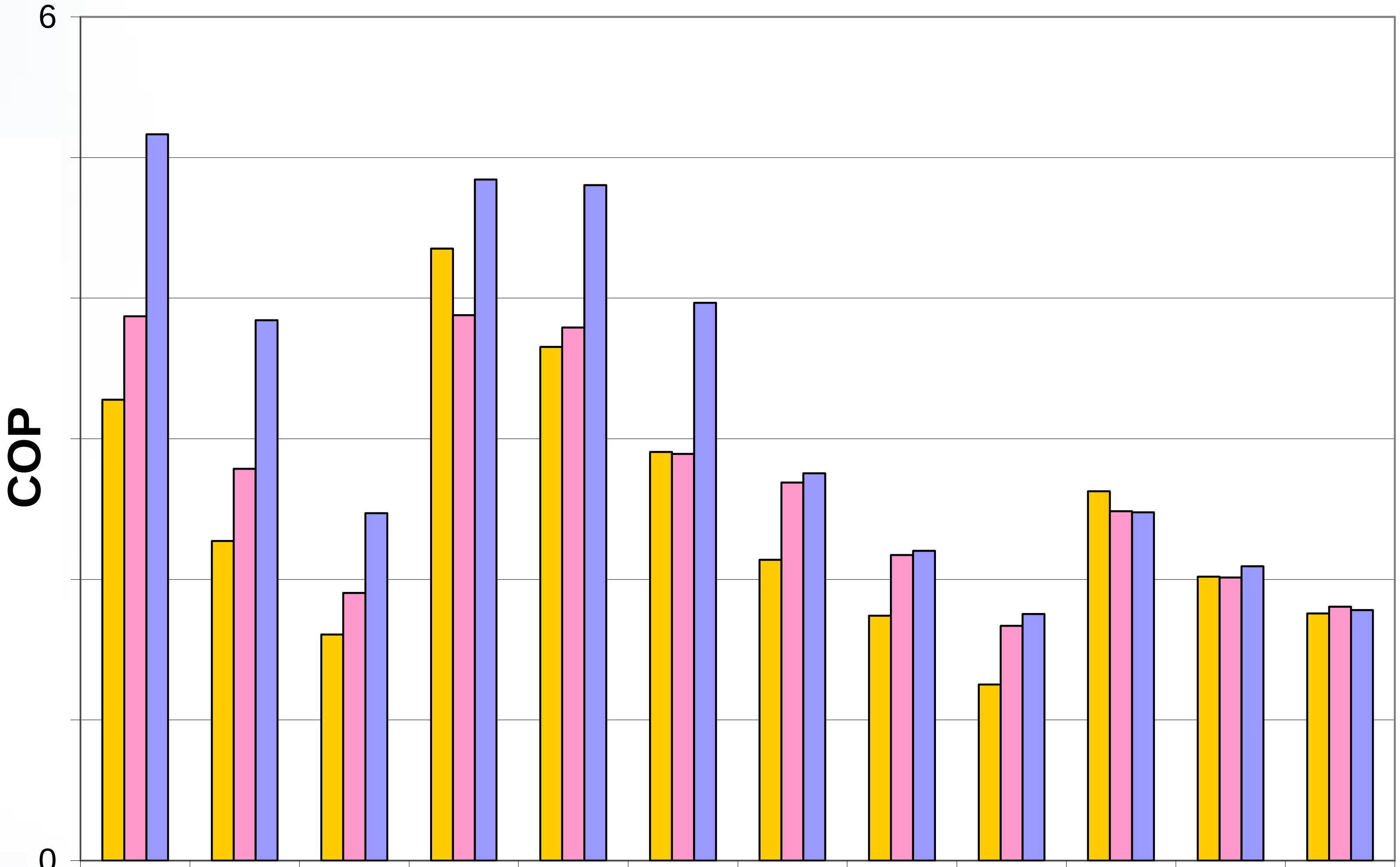
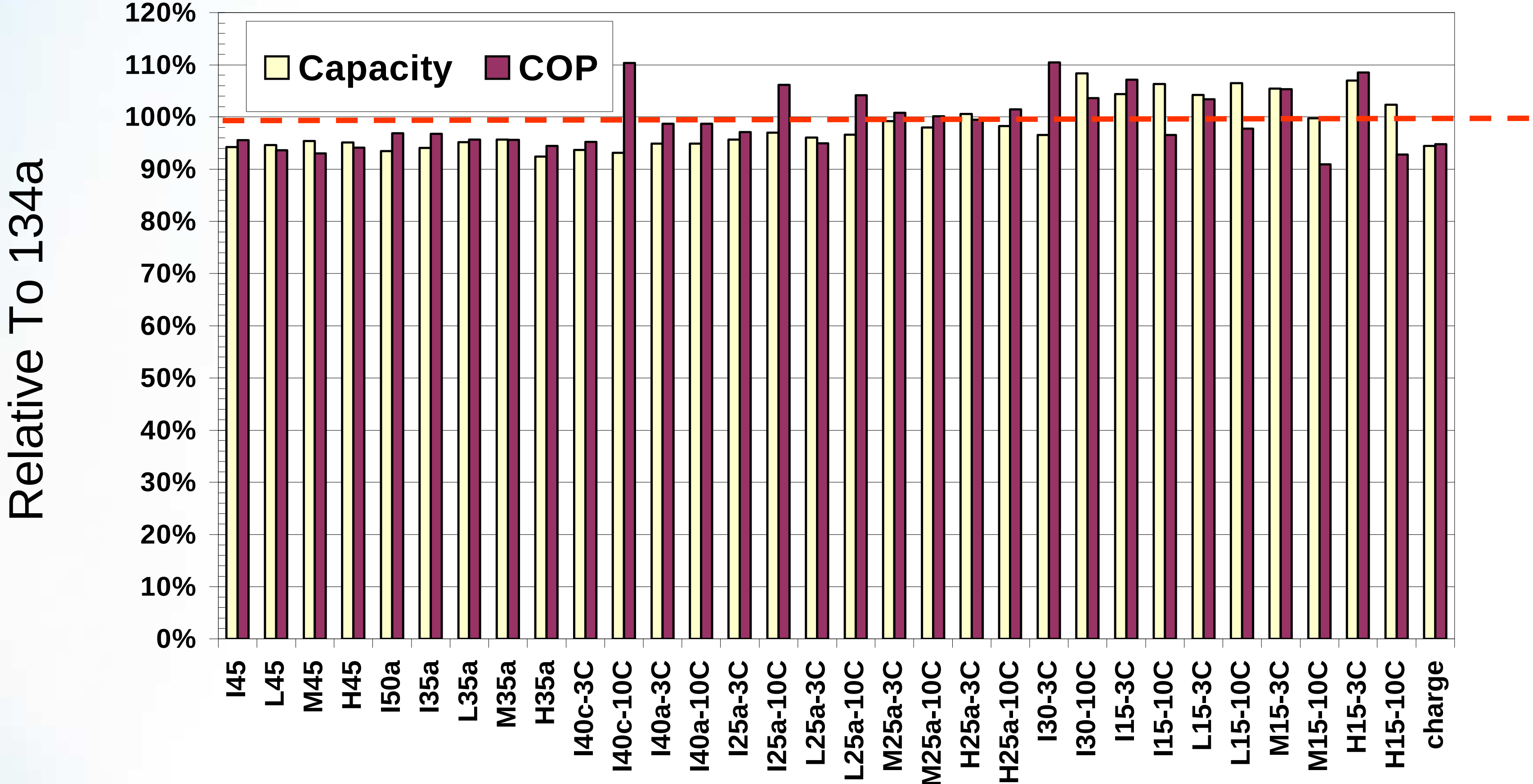
Sanden Bench Test – COP with modified TXV



	1,1	1,2	1,3	2,1	2,2	2,3	3,1	3,2	3,3	4,1	4,2	4,3
Original TXV	3,28	2,27	1,61	4,35	3,65	2,91	2,14	1,74	1,25	2,63	2,02	1,76
TXV modi. manual	3,87	2,79	1,90	3,88	3,79	2,89	2,69	2,17	1,67	2,49	2,01	1,81
TXV 2.0t Fujikoki	5,17	3,84	2,47	4,84	4,80	3,97	2,76	2,20	1,75	2,48	2,09	1,78

Additional COP improvement with modified TXV

HW/DP System Bench Test Results



No changes were made to system including TXV; Industry standard test conditions

Both Capacity and COP are generally within 5% of 134a performance.

- This was recently confirmed at two outside labs.

Lower compression ratio, low discharge temperature (12°C lower at peak conditions)

Further improvements likely with minor system optimization, for example:

- Lower ΔP suction line and / or TXV optimization to maintain a more optimum superheat.

HFO-1234yf performance is comparable to 134a; further improvement possible with minor optimization

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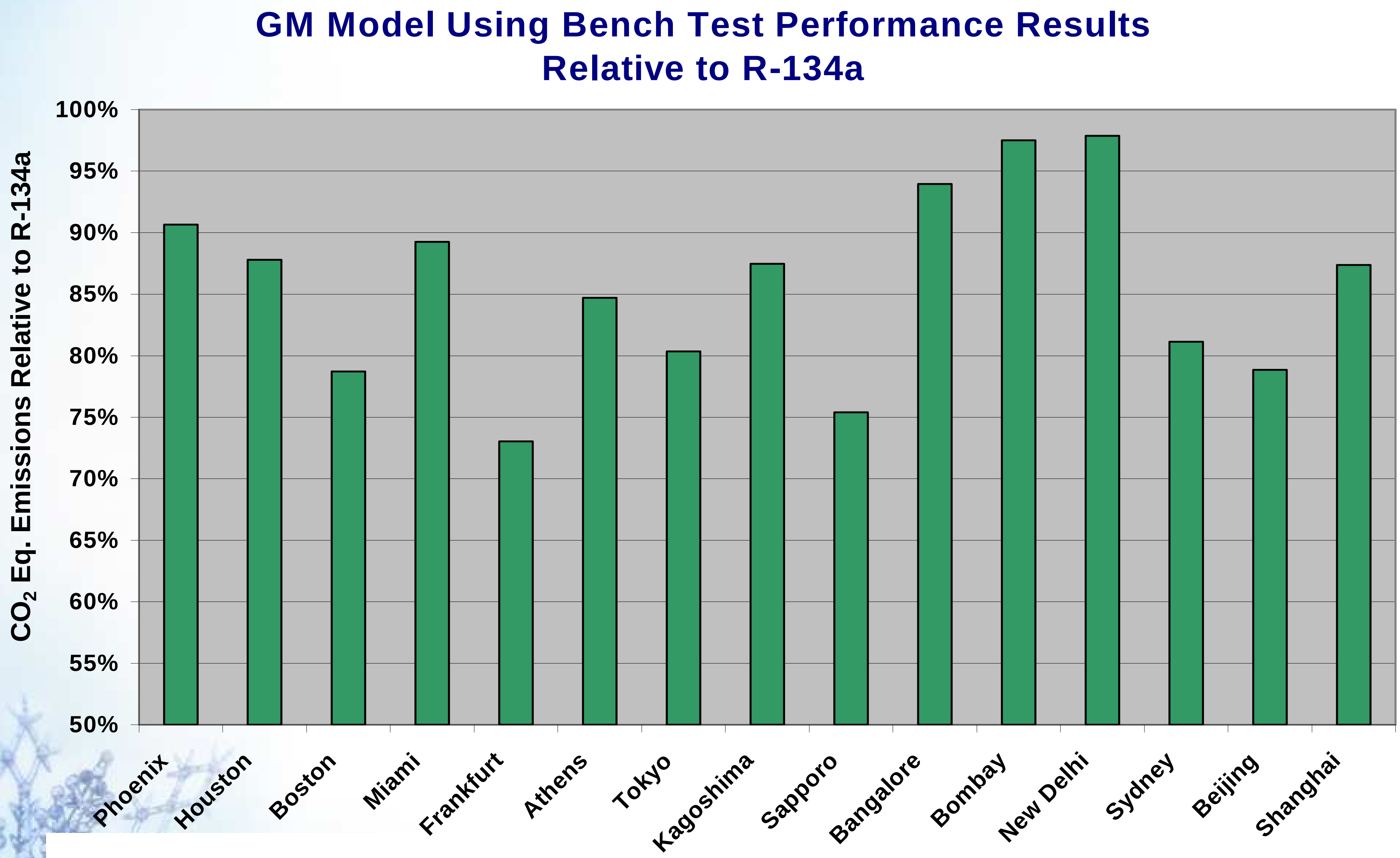
Preliminary LCCP Analysis



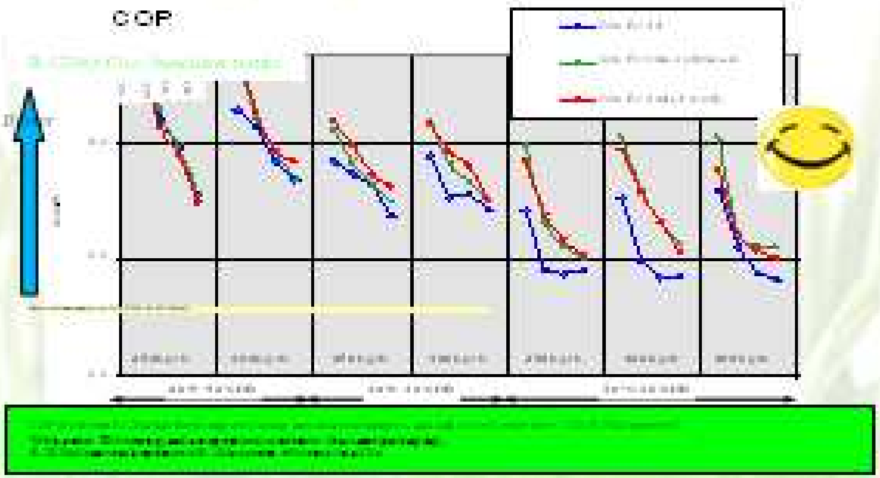
Average 15% Better LCCP Values; Up to 27% in Europe

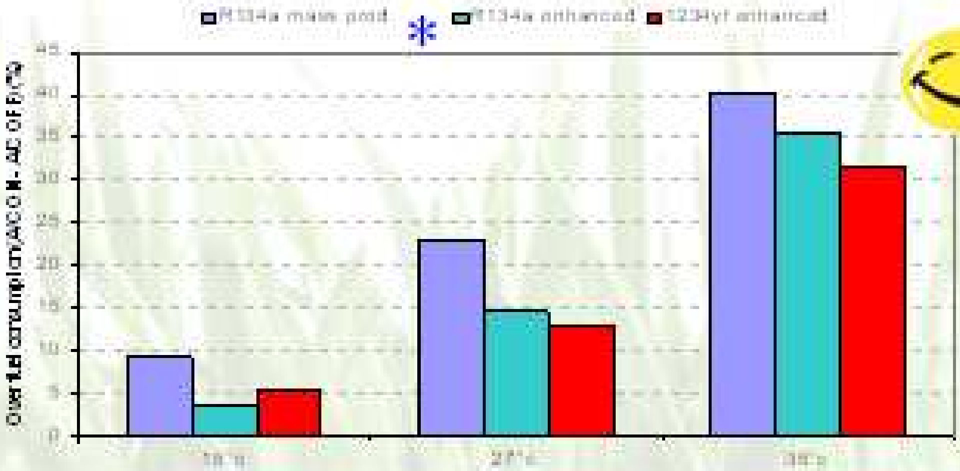
1234yf OEM Group – Fuel Consumption Testing

CCFA, JAMA, KAMA, GM / Ford / Chrysler, ANFIA, Jaguar / Land Rover, …

Is fuel consumption affected by the use of this refrigerant?

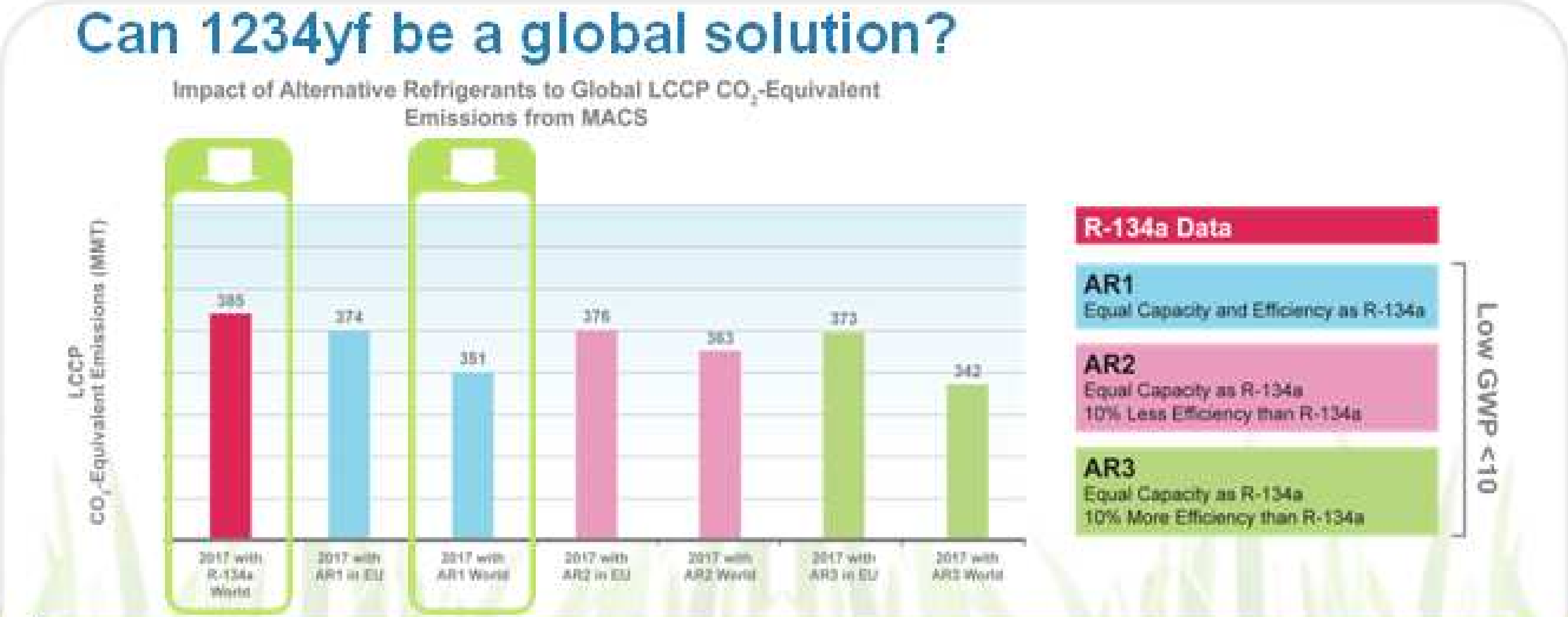
- According to the group results, by making a simple optimization of some components (condenser and TXV),
  it is easy to get same efficiency as current R-134a





1234yf OEM Group LCCP Results

ALL LIFE CYCLE (LCCP only, using GREEN-MAC-LCCP©-V3)

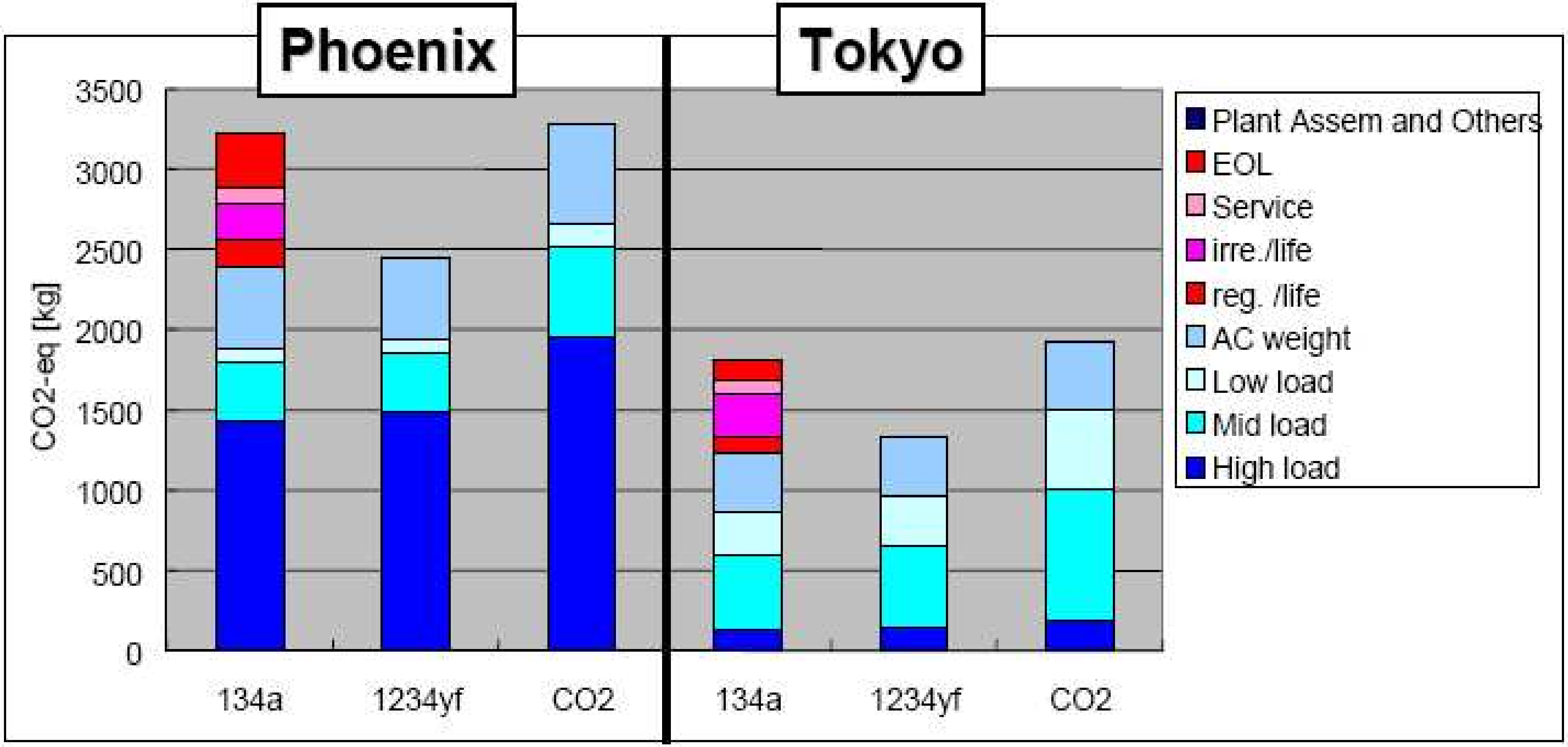


According to the OEM Group, HFO-1234yf efficiency is equal to R-134a. Expansion is possible worldwide
=> Global benefit of HFO1234yf is 8.8 %

JAMA LCCP Results

- **Emissions per vehicle, Compact Car**

> ➤**1234yf LCCP result is 20%-30% less than R134a / CO_2.**



SAE Phoenix, 2008

HFO-1234yf Handling

HFO-1234yf Will Be Handled Similar to R-134a

- **Distribution of HFO-1234yf from manufacturer to auto OEM plants and after sales service markets will be similar to R-134a**
- **Minor changes to plant charging equipment and procedures**
- **HFO-1234yf can be 100% recovered, recycled and reused on site at service shops**
- **HFO-1234yf leaks can be detected with same equipment as R-134a**
- **Unique fittings will be used ensure no cross contamination with R-134a**

Service Readiness

Service Shops

- Refrigerant for service is supplied through distributors and aftermarket channels

- Service technicians will need to have additional safety training on proper product handling/use guidelines.

- Summary of proposed modifications for HFO-1234yf automotive air-conditioning service locations
  - Recovery machines will need to be rated for flammables (non-sparking controls). Two companies already have products in development:
    - Agramkow Denmark, **http://www.agramkow.dk**
    - WAECO Germany, http://www.airconservice.de/

- Service technicians operators will need additional information regarding proper use/storage/handling of mildly flammable refrigerants
  - HFO-1234yf MSDS
  - Honeywell/DuPont Safe Handling Guidelines
  - SAE J Standards where applicable
  - Appropriate industry certification according to local/regional/country guideline

HFO-1234yf – The Leading Alternative Refrigerant to Replace R-134a

Excellent environmental properties

- Very low GWP of 4, Zero ODP, Favorable LCCP
- Atmospheric chemistry determined and published

Low toxicity, similar to R-134a

- Low acute and chronic toxicity

System performance very similar to R-134a

- Excellent COP and Capacity, no glide
  - From both internal tests and OEM tests
- Thermally stable and compatible with R-134a components
- Potential for direct substitution of R-134a

Mild flammability (manageable)

- Flammability properties significantly better than 152a; (MIE, burning velocity, etc)
- Potential for “A2L” ISO 817 classification versus “A2” for 152a based on AIST data
- Potential to use in a direct expansion A/C system

Global Solution

- Lowest total cost of transition than any alternative
- Good performance in all climates, and car sizes